

Avoiding singularity problems associated with meta-GGA (generalized gradient approximation) exchange and correlation functionals containing the kinetic energy density

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(Received 7 June 2007; accepted 25 September 2007; published online 4 December 2007)

Convergence problems of meta-GGA (generalized gradient approximation) XC (exchange and correlation) functionals containing a self-interaction correction term are traced back to a singularity of the latter that occurs at critical points of the electron density. This is demonstrated for the bond critical point of equilibrium and stretched H₂. A simple remedy is suggested that cures meta-XC functionals such as VSXC, TPSS, M05, M06, and their derivatives without extra cost. © 2007 American Institute of Physics. [DOI: 10.1063/1.2800011]

I. INTRODUCTION

Density-functional theory¹ (DFT) calculations using meta-GGA (generalized gradient approximation) functionals (see, e.g., Refs. 2–6) for the exchange and correlation (XC) energy have attracted intense interest recently. We report here that calculations with commonly used meta-GGA XC functionals such as VSXC,² TPSS,³ PKZB,⁴ M05,⁵ M05-2X,⁵ or M06-L (Ref. 6) can lead to convergence problems in the self-consistent-field (SCF) iteration caused by a singularity in the self-interaction correction term containing the kinetic energy density. These problems in turn influence the structure optimization, which can lead to erroneous geometries. We observed this problem first for the M05 XC (Ref. 5) description of the H₂ molecule. Calculation of the dissociation curve for either ground or excited states leads to erratic results unless an extremely fine benchmark grid is used for the numerical integration of the XC terms. In the case mentioned, the iteration converges properly for certain values of the bond distance $R=R(\text{H},\text{H})$, whereas it diverges altogether or converges to an incorrect configuration, e.g., the $(1\sigma_u)^2$ configuration, for other R values. The convergence or divergence behavior in dependence on R follows no clear pattern. In the course of the investigation, we found that similar problems for other meta-GGA functionals are encountered for molecules which are generally considered as typical benchmark cases.

For the practicability of an XC functional, it is problematic when convergence problems occur already for simple reference systems. A detailed analysis reveals that these convergence problems are related to the equal-spin part of the correlation energy in the meta-GGA functional considered. Based on this analysis, we suggest in the present work a

modification of the functionals that improves their numerical stability in SCF iterations while leaving the resulting XC energies essentially unchanged. The suggested modification is easy to implement for the functionals under consideration and does not imply a substantial extra computational cost.

The paper is organized as follows. In Sec. II, we present the analysis of the convergence problems and describe a remedy of the XC functionals so that the singularity problems vanish. Section III summarizes the computational details of this work and in Sec. IV a number of molecules are described for which the meta-GGA XC functionals mentioned above lead to erratic results. Section V presents a brief summary.

II. THEORY

In the meta-GGA functionals under investigation, the correlation energy is decomposed into an equal-spin and an opposite-spin component. The expression for the equal-spin correlation for spin orientation σ ($\sigma=\alpha$ or β) contains the factor

$$D_\sigma = 1 - \frac{\gamma_\sigma}{4\rho_\sigma\tau_\sigma}, \quad (1a)$$

$$\gamma_\sigma = |\nabla\rho_\sigma|^2, \quad (1b)$$

$$\tau_\sigma = \sum_i^{\text{occ}} |\nabla\varphi_{i\sigma}|^2, \quad (1c)$$

for the elimination of self-interaction errors in the correlation energy. We note that $\tau_\sigma=0$ implies $\gamma_\sigma=0$ but not vice versa. At positions where only one electron of spin σ is present (called “one-electron positions” in the following),

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$$\gamma_\sigma = 4\rho_\sigma\tau_\sigma, \quad (2)$$

so that D_σ and the contribution to the correlation energy become zero.

The Kohn-Sham (KS) matrix elements used in the SCF iterations depend on the derivatives of D_σ with respect to ρ_σ , γ_σ , and τ_σ , where the latter are

$$\frac{\partial D_\sigma}{\partial \gamma_\sigma} = -\frac{1}{4\rho_\sigma\tau_\sigma}, \quad (3a)$$

$$\frac{\partial D_\sigma}{\partial \tau_\sigma} = \frac{\gamma_\sigma}{4\rho_\sigma\tau_\sigma^2}. \quad (3b)$$

Note that at one-electron positions, $\partial D_\sigma/\partial \tau_\sigma = 1/\tau_\sigma$ because of Eq. (2). If ρ_σ has a stationary point that is a one-electron position as, e.g., the bond center of the H_2 molecule, then $\tau_\sigma = 0$ at this point (provided that $\rho_\sigma \neq 0$ at this point). Also, for small distances x from the stationary point, $\gamma_\sigma \propto x^2$, $\tau_\sigma \propto x^2$. Consequently, both derivatives $\partial D_\sigma/\partial \gamma_\sigma$ and $\partial D_\sigma/\partial \tau_\sigma$ have a $1/x^2$ singularity at that point. The elements μ, ν of the XC parts of the Fock matrices are given by Eq. (4),⁷

$$F_{\mu\nu}^{XC\sigma} = \int \left[\frac{\partial f}{\partial \rho_\sigma} \phi_\mu \phi_\nu + \left(2 \frac{\partial f}{\partial \gamma_\sigma} \nabla \rho_\sigma + \frac{\partial f}{\partial \gamma_{\sigma\sigma'}} \nabla \rho_{\sigma'} \right) \nabla (\phi_\mu \phi_\nu) + 2 \frac{\partial f}{\partial \tau_\sigma} \nabla \phi_\mu \nabla \phi_\nu \right] d^3r, \quad (4)$$

where f gives the functional dependence of the XC energy density on ρ_σ , γ_σ , $\gamma_{\sigma\sigma'}$, and τ_σ , respectively, and $\gamma_{\sigma\sigma'} = \nabla \rho_\sigma \nabla \rho_{\sigma'}$. The singularities in $\partial D_\sigma/\partial \gamma_\sigma$ and $\partial D_\sigma/\partial \tau_\sigma$ also occur in $\partial f/\partial \gamma_\sigma$ and $\partial f/\partial \tau_\sigma$. Despite the presence of these $1/x^2$ singularities at the stationary point, this integral still converges. However, when integrating numerically, the integral is replaced by a finite sum of the form

$$F_{\mu\nu}^{XC\sigma} \approx \sum_i [\dots]_i \Delta^3 r_i, \quad (5)$$

where $\Delta^3 r_i$ is the finite volume element and the dots represent all terms in the square brackets of Eq. (4) evaluated at the grid point \mathbf{r}_i . If \mathbf{r}_i happens to be close to the stationary point in ρ_σ , then the value of $[\dots]_i$ will be large, and the contribution of volume element i to $F_{\mu\nu}^{XC\sigma}$ will be exaggerated. This exaggeration will be more serious the larger $\Delta^3 r_i$ is, i.e., the coarser the integration grid is. The exaggerated terms in the KS matrix, in turn, cause the convergence problems mentioned. That is, *the use of the meta-GGA functionals under consideration can lead to convergence problems if the system in question has a stationary point in its density ρ_σ that is a one-electron position for σ (unless this point is in a nodal surface of ρ_σ)*. Thus, if there is only one electron for one of the spin orientation σ , then any stationary point in ρ_σ can cause convergence problems of the kind observed. This is in line with the observations made for the H_2 and other molecules as will be described in Sec. IV.

The analysis of the convergence problems leads to two conclusions with regard to their properties: First, the problems occur when a point of the integration grid is close to a

stationary point of ρ_σ as, e.g., the bond center of H_2 . This explains the erratic occurrence of the convergence problems. If, for instance, one performs a potential-energy scan for H_2 by increasing $R=R(H,H)$ in very small steps, the convergence problems will occur every time if one of the grid points passes the bond center. For usual production grids, the radial distance between neighboring grid points in the valence region is of the order of 0.1 bohr radii. That is, R intervals with proper SCF convergence and with convergence problems would alternate on a scale of about 0.1 bohr. A production potential energy scan with a step length of 0.1 bohr or more will then scan the two kinds of intervals in random order thus leading to an erratic description. A geometry optimization will abort if one of the intermediate geometries belongs to an R interval with convergence problems.

Second, the convergence behavior for a given system may depend not only on the current geometry and the level of theory used (i.e., XC functional and integration grid) but also on the algorithm and parameters used for the SCF iteration.

It is easy to predict under which circumstances the convergence problems should not occur. If bonding and antibonding orbitals are occupied, as in the case of the He_2 dimer, $\tau_\sigma > 0$ will hold everywhere in the molecule, including the bond center, and the singularity in the KS matrix will be suppressed. Likewise, core electrons will largely suppress the occurrence of singularities. For the Li_2 dimer, for instance, the core electrons will generate a small but significant positive τ_σ value at the bond center, which prevents the KS matrix elements from becoming singular. It might thus appear that the convergence problems appear only for a small class of molecules and are of minor importance. However, on the one hand, it will be a potential source of problems if an XC functional behaves erratically even for simple molecules, which in addition are often needed as references in chemical investigations. Besides, the convergence problems can also occur for molecules with heavier atoms if the core electrons are described by effective core potentials (ECPs). Thus, it is desirable to remedy the convergence problems by a suitable modification of the functionals.

The numerical problem mentioned affects only the derivatives of D_σ (and eventually the KS matrix) rather than the values of D_σ (and thus eventually the equal spin correlation density) itself. More specifically, the values of D_σ for physically relevant sets of values ρ_σ , γ_σ , and τ_σ are reasonable. The problems arise from the behavior of D_σ for unphysical sets of values (e.g., $\tau_\sigma = 0$ but $\gamma_\sigma \neq 0$), which are not relevant for the calculation of the correlation energy itself but are probed during the calculation of the derivatives of D_σ . That is, if the SCF iteration converges to the proper state, the calculated energy will be reliable. Consequently, a modification of the functionals has to be done in a way that the values of D_σ for physically relevant cases are changed as little as possible, whereas the singular behavior of the derivatives has to be suppressed. In other words, the improvement of the meta-GGA XC functionals from Refs. 2–6 given above should not modify the calculated XC energy values for those cases where the functionals from Refs. 2–6 in their original form work properly in the SCF iteration.

TABLE I. Absolute energies of $\text{H}_2(^1\Sigma_g^+)$ in Hartree calculated for different distances $R(\text{H},\text{H})$ with different integration grids at M05/6-311++(2*p*) using the unmodified and modified M05 functional. The (75,302), (99,590), and (96,32,64) grids correspond to fine production grids, very fine production grids, and benchmark grids in standard DFT programs. $R=R(\text{H},\text{H})$ given in bohr units. Equilibrium bond distance of 1.403 bohr units.

| <i>R</i> | M05 | | | Modified M05 ($a=10^{-4}$ a.u.) | | |
|----------|-------------------|-------------------|---------------------|----------------------------------|-------------------|---------------------|
| | <i>E</i> (75,302) | <i>E</i> (99,590) | <i>E</i> (96,32,64) | <i>E</i> (75,302) | <i>E</i> (99,590) | <i>E</i> (96,32,64) |
| 1.0 | 7.955 388 30 | -1.118 217 22 | -1.118 217 22 | -1.118 216 94 | -1.118 217 22 | -1.118 217 22 |
| 1.1 | -1.143 995 61 | -1.143 995 96 | -1.143 995 98 | -1.143 995 61 | -1.143 995 96 | -1.143 995 98 |
| 1.2 | -1.158 966 60 | -1.158 966 60 | -1.158 966 60 | -1.158 966 60 | -1.158 966 60 | -1.158 966 60 |
| 1.3 | -1.166 416 33 | -1.166 416 08 | -1.166 416 07 | -1.166 416 33 | -1.166 416 08 | -1.166 416 07 |
| 1.4 | -1.168 594 57 | -1.168 594 40 | -1.168 594 41 | -1.168 594 57 | -1.168 594 40 | -1.168 594 41 |
| 1.5 | -1.167 046 92 | -1.167 047 05 | -1.167 047 07 | -1.167 046 92 | -1.167 047 05 | -1.167 047 07 |
| 1.6 | -1.162 839 30 | -1.162 839 56 | -1.162 839 57 | -1.162 839 30 | -1.162 839 56 | -1.162 839 57 |
| 1.7 | -1.156 715 07 | Not converged | -1.156 715 29 | -1.156 715 07 | -1.156 715 29 | -1.156 715 29 |
| 1.8 | 8.198 001 81 | -1.149 208 97 | -1.149 208 96 | -1.149 208 73 | -1.149 208 97 | -1.149 208 96 |
| 1.9 | -1.140 724 11 | -1.140 724 46 | -1.140 724 46 | -1.140 724 11 | -1.140 724 46 | -1.140 724 46 |
| 2.0 | 7.688 319 07 | 7.688 299 90 | -1.131 582 19 | -1.131 581 84 | -1.131 582 19 | -1.131 582 19 |
| 2.1 | -1.122 043 46 | -1.122 043 62 | -1.122 043 63 | -1.122 043 46 | -1.122 043 62 | -1.122 043 63 |
| 2.2 | -1.112 322 10 | -1.112 321 87 | -1.112 321 87 | -1.112 322 10 | -1.112 321 87 | -1.112 321 87 |
| 2.3 | -1.102 587 17 | -1.102 586 57 | -1.102 586 57 | -1.102 587 17 | -1.102 586 57 | -1.102 586 57 |
| 2.4 | -1.092 968 98 | -1.092 968 11 | -1.092 968 11 | -1.092 968 98 | -1.092 968 11 | -1.092 968 11 |
| 2.5 | -1.083 562 50 | -1.083 561 93 | -1.083 561 92 | -1.083 562 50 | -1.083 561 93 | -1.083 561 92 |

As the analysis reveals that the convergence problems arise from one-electron positions, the contributions to the equal-spin correlation energy have to vanish anyway, i.e., $D_\sigma=0$. An obvious solution to the problem is thus to exclude all grid points from the numerical integration for which τ_σ is below a certain threshold. However, such cutoff procedures can give rise to new problems, e.g., discontinuities in potential-energy surfaces and energy gradients and, consequently, problems in geometry optimizations. A more appropriate approach is to modify the expression for D_σ in a way that the value of the equal-spin correlation is essentially unaffected, however, the singularities in $\partial D_\sigma/\partial\gamma_\sigma$ and $\partial D_\sigma/\partial\tau_\sigma$ are eliminated. This can be accomplished by replacing D_σ by \tilde{D}_σ ,

$$\tilde{D}_\sigma = \underbrace{(1 - e^{-\tau_\sigma^2/a^2})}_{=T_\sigma} D_\sigma. \quad (6)$$

Here, a is a parameter responsible for damping irregularities in the value of D_σ . For $\tau_\sigma \gg a$, $\tilde{D}_\sigma \approx D_\sigma$, i.e., the correlation energy contribution is not affected by T_σ . Only for small τ_σ (with reference to a) does T_σ influence the value of \tilde{D}_σ . Small τ_σ values are indicative of one-electron positions where equal-spin electron correlation is not present anyway. One can easily verify that T_σ eliminates the $1/\tau_\sigma$ singularities in $\partial D_\sigma/\partial\gamma_\sigma$ and $\partial D_\sigma/\partial\tau_\sigma$ given in Eqs. (3a) and (3b).

The parameter a must be chosen large enough to safely suppress the singularities in $\partial D_\sigma/\partial\gamma_\sigma$ and $\partial D_\sigma/\partial\tau_\sigma$ but small enough to avoid an impact of the equal-spin correlation energy. We determined the factor a by a series of test calculations, which are described and discussed in the following sections.

III. COMPUTATIONAL DETAILS

We implemented the modified M05 functional into the program package COLOGNE07⁸ and tested it for a number of

molecules employing Pople's 6-311++G(2*d*,2*p*) basis set.⁹ For heavy atom systems, we used also the Stuttgart/Dresden ECP10SDF effective core potential and the corresponding basis sets.¹⁰ The following integration grids were used: (i) an Euler-MacLaurin/Lebedev (75,302) integration grid,^{11,12} corresponding to fine production grids in modern quantum-chemistry packages, (ii) an Euler-MacLaurin/Lebedev (99,590) grid, corresponding to ultrafine production grids, and (iii) an Euler-MacLaurin/spherical (96,32,64) grid, characteristic for a benchmark grid.

Test calculations for H_2 and H_2O were performed to determine the optimal parameter a in Eq. (6). This value was then applied for all other molecules investigated.

For all molecules investigated, we performed geometry scans with both the unmodified and the modified meta-GGA functionals mentioned above, employing the three grids where we focus in this work on the results obtained for the M05 functional. Similar observations and results were obtained for the other functionals.

IV. RESULTS

Table I lists results for potential energy scans of H_2 with R varying from 1 to 2.5 bohrs in steps of 0.1 bohr, employing both the unmodified and the modified M05 functionals and the three integration grids described in Sec. III. For the unmodified functional and the (75,302) grid, one obtains unreasonable energy values above 7 hartrees for 1.0, 1.8, and 2.0 bohrs, indicating that the SCF procedure converges to an incorrect state. For the finer (99,590) grid, the energy is unreasonable for $R=2.0$ bohrs (7.688 hartree); besides, the SCF procedure diverges for $R=1.7$ bohr. For the (96,32,64) reference grid, all energy values are in the interval of -1.169 to -1.083 hartree, i.e., an interval about 5 kcal/mol above the ground-state energy, indicating that there are no

TABLE II. Absolute energies of $\text{H}_2^+(^2\Sigma_g^+)$ in Hartree calculated for different distances $R(\text{H},\text{H})$ with different integration grids at M05/6-311++(2p) using the unmodified and modified M05 functional. The (75,302), (99,590), and (96,32,64) grids correspond to fine production grids, very fine production grids, and benchmark grids in standard DFT programs. $R=R(\text{H},\text{H})$ given in bohr units. Equilibrium bond distance of 2.092 bohr units.

| R | M05 | | | Modified M05 ($a=10^{-4}$ a.u.) | | |
|-----|---------------|---------------|---------------|----------------------------------|---------------|---------------|
| | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ |
| 1.0 | -0.449 599 41 | -0.449 101 80 | -0.449 101 67 | -0.449 599 35 | -0.449 101 76 | -0.449 101 67 |
| 1.1 | 3.780 313 01 | -0.494 248 01 | -0.494 248 13 | -0.494 492 98 | -0.494 247 99 | -0.494 248 13 |
| 1.2 | -0.527 360 25 | -0.527 305 11 | -0.527 304 98 | -0.527 360 17 | -0.527 305 11 | -0.527 304 98 |
| 1.3 | -0.551 528 00 | -0.551 602 50 | -0.551 602 22 | -0.551 527 92 | -0.551 602 36 | -0.551 602 22 |
| 1.4 | -0.569 295 70 | -0.569 451 27 | -0.569 451 23 | -0.569 295 52 | -0.569 451 27 | -0.569 451 23 |
| 1.5 | -0.582 278 87 | -0.582 486 14 | -0.582 486 11 | -0.582 278 87 | -0.582 486 14 | -0.582 486 11 |
| 1.6 | -0.591 642 28 | -0.591 879 45 | -0.591 879 41 | -0.591 642 20 | -0.591 879 45 | -0.591 879 41 |
| 1.7 | -0.598 233 57 | 3.624 947 00 | -0.598 479 44 | -0.598 233 57 | -0.598 479 49 | -0.598 479 44 |
| 1.8 | 3.903 849 71 | -0.602 908 15 | -0.602 908 10 | -0.602 674 02 | -0.602 908 15 | -0.602 908 10 |
| 1.9 | -0.605 430 32 | -0.605 635 90 | -0.605 635 87 | -0.605 430 32 | -0.605 635 90 | -0.605 635 87 |
| 2.0 | 3.635 116 80 | 3.636 130 33 | -0.607 032 96 | -0.606 867 89 | -0.607 032 98 | -0.607 032 96 |
| 2.1 | -0.607 278 99 | -0.607 398 01 | -0.607 398 00 | -0.607 278 99 | -0.607 398 01 | -0.607 398 00 |
| 2.2 | -0.606 896 75 | 3.644 321 85 | -0.606 972 31 | -0.606 896 75 | -0.606 972 32 | -0.606 972 31 |
| 2.3 | -0.605 906 73 | -0.605 948 75 | -0.605 948 73 | -0.605 906 73 | -0.605 948 75 | -0.605 948 73 |
| 2.4 | -0.604 458 78 | -0.604 479 34 | -0.604 479 32 | -0.604 458 77 | -0.604 479 33 | -0.604 479 31 |
| 2.5 | -0.602 677 28 | -0.602 686 40 | -0.602 686 38 | -0.602 677 28 | -0.602 686 40 | -0.602 686 38 |

convergence problems and one obtains a smooth dissociation curve for the (96,32,64) grid. In those cases where no convergence problems occur, the energy values for a given R value and different grids agree within 10^{-6} hartree. The results for the unmodified functional confirm that the M05 functional leads to erratic convergence behavior for the H_2 molecule. Noteworthy is that one may obtain convergence problems for a finer grid [$R=1.7$ bohrs and (99,590) grid] in cases where a coarser grid provides a convergent SCF procedure.

The modified M05 functional ($a=10^{-4}$ a.u., Table I) provides smooth dissociation curves for all three grids. In those cases where the original M05 functional leads to SCF convergence, the unmodified and modified M05 functionals pro-

vide energies differing by less than 10^{-7} hartree. In line with this fact, the three grids used will provide energies differing at most by 10^{-6} hartree for a given geometry if the modified M05 functional is used.

The results for H_2 demonstrate that the modified M05 functional eliminates the convergence problems observed for the original M05 functional in the case of H_2 . In addition, the results from the unmodified and modified M05 functionals agree, i.e., the modification does not generate any undesirable changes in the behavior of the M05 functional.

The convergence problems described should occur in all molecules with only one electron for one of the spin orientations. We have verified this hypothesis by performing potential scans for molecules such as H_2^+ (Table II), He_2^+ (Table

TABLE III. Absolute energies of $\text{He}_2^+(^1\Sigma_g^+)$ in Hartree calculated for different distances $R(\text{He},\text{He})$ with different integration grids at M05/6-311++(2p) using the unmodified and modified M05 functional. The (75,302), (99,590), and (96,32,64) grids correspond to fine production grids, very fine production grids, and benchmark grids in standard DFT programs. $R=R(\text{He},\text{He})$ given in bohr units. Equilibrium bond distance of 1.327 bohr units.

| R | M05 | | | Modified M05 ($a=10^{-4}$ a.u.) | | |
|-----|---------------|---------------|---------------|----------------------------------|---------------|---------------|
| | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ |
| 1.0 | -3.593 108 16 | Not converged | -3.593 512 29 | -3.593 108 17 | -3.593 512 41 | -3.593 512 29 |
| 1.1 | -3.644 952 94 | -3.645 310 24 | -3.645 310 17 | -3.644 952 94 | -3.645 310 25 | -3.645 310 17 |
| 1.2 | -3.670 519 90 | -3.670 768 46 | -3.670 768 44 | -3.670 519 90 | -3.670 768 46 | -3.670 768 44 |
| 1.3 | 4.483 775 46 | -3.679 439 86 | -3.679 439 85 | -3.679 294 66 | -3.679 439 86 | -3.679 439 85 |
| 1.4 | -3.677 502 24 | -3.677 605 18 | -3.677 605 12 | -3.677 502 24 | -3.677 605 18 | -3.677 605 12 |
| 1.5 | -3.669 234 85 | -3.669 354 07 | -3.669 354 04 | -3.669 234 85 | -3.669 354 08 | -3.669 354 04 |
| 1.6 | -3.657 198 82 | -3.657 354 68 | -3.657 354 73 | -3.657 198 82 | -3.657 354 68 | -3.657 354 73 |
| 1.7 | -3.643 216 77 | -3.643 415 53 | -3.643 415 29 | -3.643 216 77 | -3.643 415 53 | -3.643 415 29 |
| 1.8 | -3.628 573 09 | -3.628 791 34 | -3.628 792 62 | -3.628 573 09 | -3.628 791 34 | -3.628 792 62 |
| 1.9 | -3.614 040 25 | -3.614 293 11 | -3.614 290 72 | -3.614 040 25 | -3.614 293 11 | -3.614 290 72 |
| 2.0 | -3.600 193 46 | -3.600 369 89 | -3.600 371 49 | -3.600 193 45 | -3.600 369 87 | -3.600 371 47 |

TABLE IV. Absolute energies of $H_3^+(^1A_1')$ in Hartree calculated for different distances $R(H,H)$ with different integration grids at M05/6-311++(2p) using the unmodified and modified M05 functional. The (75,302), (99,590), and (96,32,64) grids correspond to fine production grids, very fine production grids, and benchmark grids in standard DFT programs. $R=R(H,H)$ given in bohr units. Equilibrium bond distance of 1.542 bohr units.

| R | M05 | | | Modified M05 ($a=10^{-4}$ a.u.) | | |
|-----|---------------|---------------|---------------|----------------------------------|---------------|---------------|
| | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ |
| 1.0 | -1.127 294 15 | -1.127 098 12 | -1.127 096 12 | -1.127 294 15 | -1.127 098 12 | -1.127 096 12 |
| 1.1 | -1.211 636 38 | -1.211 606 14 | -1.211 604 54 | -1.211 636 38 | -1.211 606 14 | -1.211 604 53 |
| 1.2 | -1.267 645 02 | -1.267 712 84 | -1.267 710 56 | -1.267 645 02 | -1.267 713 09 | -1.267 710 55 |
| 1.3 | -1.303 840 93 | -1.303 965 31 | -1.303 961 22 | -1.303 840 92 | -1.303 965 12 | -1.303 961 22 |
| 1.4 | -1.326 012 88 | 7.880 962 26 | -1.326 164 19 | -1.326 012 87 | -1.326 167 16 | -1.326 164 18 |
| 1.5 | -1.338 152 29 | 7.823 359 56 | -1.338 327 31 | -1.338 152 29 | -1.338 328 76 | -1.338 327 31 |
| 1.6 | -1.342 987 79 | 7.924 988 87 | -1.343 180 41 | -1.342 987 54 | -1.343 181 63 | -1.343 180 41 |
| 1.7 | -1.342 587 80 | -1.342 786 15 | -1.342 784 58 | -1.342 587 51 | -1.342 785 89 | -1.342 784 58 |
| 1.8 | 5.264 007 93 | -1.338 660 38 | -1.338 659 01 | -1.338 477 27 | -1.338 660 23 | -1.338 659 01 |
| 1.9 | 6.597 368 13 | -1.331 880 97 | -1.331 879 88 | -1.331 731 19 | -1.331 880 89 | -1.331 879 88 |
| 2.0 | 6.839 897 06 | 6.266 742 89 | -1.323 162 68 | -1.323 056 31 | -1.323 163 43 | -1.323 162 68 |
| 2.1 | -1.312 953 21 | -1.313 019 67 | -1.313 018 87 | -1.312 952 93 | -1.313 019 34 | -1.313 018 87 |
| 2.2 | 6.679 557 85 | -1.301 859 38 | -1.301 858 02 | -1.301 823 05 | -1.301 858 23 | -1.301 858 02 |
| 2.3 | -1.289 998 37 | -1.290 013 69 | -1.290 012 52 | -1.289 997 37 | -1.290 012 41 | -1.290 012 51 |
| 2.4 | -1.277 745 37 | -1.277 748 77 | -1.277 747 67 | -1.277 743 91 | -1.277 747 21 | -1.277 747 65 |
| 2.5 | 5.576 056 88 | -1.265 278 56 | -1.265 277 88 | -1.265 280 09 | -1.265 276 96 | -1.265 277 82 |

III), and H_3^+ (Table IV). In analogy to the case of H_2 , one finds spurious cases of convergence to an incorrect state or SCF divergence for the (75,302) and (99,590) grids. Only for the (96,32,64) grid do convergence problems not arise. In line with the observations made for H_2 (Table I), the modification of the M05 functional satisfactorily corrects the erroneous convergence behavior in all cases.

Systems containing alkali atoms should be prone to the same convergence problems if described with pseudopotentials. For the purpose of testing this hypothesis, we performed a potential-energy scan for the Na dimer described with the Stuttgart/Dresden SDF ECP and the corresponding valence basis set.¹⁰ Table V shows the absolute energies for R values in the range from 6.0 to 8.0 bohrs. Indeed, for the

TABLE V. Absolute energies of $Na_2(^1\Sigma_g^+)$ in Hartree calculated for different distances $r(Na,Na)$ with different integration grids at M05/ECP10SDF using the unmodified and modified M05 functional. The (75,302), (99,590), and (96,32,64) grids correspond to fine production grids, very fine production grids, and benchmark grids in standard DFT programs. $R=R(H,H)$ given in bohr units. Equilibrium distance: 6.067 bohr units for (75,302) grid, 6.079 bohr units for (99,590) grid, and 6.049 bohr units for (96,32,64) grid.

| R | M05 | | | Modified M05 ($a=10^{-4}$ a.u.) | | |
|-----|---------------|---------------|---------------|----------------------------------|---------------|---------------|
| | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ | $E(75,302)$ | $E(99,590)$ | $E(96,32,64)$ |
| 6.0 | -0.383 680 70 | -0.383 441 81 | -0.383 651 58 | -0.383 680 70 | -0.383 441 81 | -0.383 651 58 |
| 6.1 | -0.383 694 27 | -0.383 470 42 | -0.383 650 68 | -0.383 694 27 | -0.383 470 42 | -0.383 650 68 |
| 6.2 | -0.383 634 54 | -0.383 404 55 | -0.383 554 61 | -0.383 634 54 | -0.383 404 55 | -0.383 554 61 |
| 6.3 | -0.383 479 31 | -0.383 253 74 | -0.383 376 66 | -0.383 479 31 | -0.383 253 74 | -0.383 376 66 |
| 6.4 | -0.383 218 82 | 0.037 739 23 | -0.383 121 87 | -0.383 218 82 | -0.383 021 76 | -0.383 121 87 |
| 6.5 | -0.382 886 60 | -0.382 715 74 | -0.382 795 35 | -0.382 886 60 | -0.382 715 74 | -0.382 795 35 |
| 6.6 | 0.325 725 90 | -0.382 346 72 | -0.382 407 19 | -0.382 512 71 | -0.382 346 72 | -0.382 407 19 |
| 6.7 | -0.045 474 68 | -0.381 918 76 | -0.381 963 16 | -0.382 084 59 | -0.381 918 76 | -0.381 963 16 |
| 6.8 | -0.381 583 70 | -0.381 433 73 | -0.381 466 17 | -0.381 583 70 | -0.381 433 73 | -0.381 466 17 |
| 6.9 | -0.381 024 94 | 0.084 766 81 | -0.380 922 18 | -0.381 024 94 | -0.380 901 38 | -0.380 922 18 |
| 7.0 | -0.380 439 46 | -0.094 989 97 | -0.380 336 51 | -0.380 439 46 | -0.380 329 70 | -0.380 336 51 |
| 7.1 | 0.147 220 93 | Not converged | -0.379 711 89 | -0.379 834 01 | -0.379 717 53 | -0.379 711 89 |
| 7.2 | Not converged | Not converged | -0.379 052 19 | -0.379 188 78 | -0.379 066 94 | -0.379 052 19 |
| 7.3 | 0.221 227 18 | 0.191 661 41 | -0.378 361 17 | -0.378 496 79 | -0.378 388 16 | -0.378 361 17 |
| 7.4 | 0.237 145 00 | Not converged | -0.377 640 72 | -0.377 775 23 | -0.377 684 78 | -0.377 640 72 |
| 7.5 | 0.099 827 68 | 0.235 827 10 | -0.376 893 24 | -0.377 042 89 | -0.376 951 94 | -0.376 893 24 |
| 7.6 | 0.095 785 15 | 0.219 355 01 | -0.376 123 00 | -0.376 299 98 | -0.376 191 72 | -0.376 123 00 |
| 7.7 | 0.198 903 72 | 0.219 765 12 | -0.375 331 10 | -0.375 528 28 | -0.375 413 74 | -0.375 331 10 |
| 7.8 | 0.252 009 59 | 0.234 029 53 | -0.374 516 90 | -0.374 721 42 | -0.374 618 99 | -0.374 516 90 |
| 7.9 | Not converged | 0.057 852 51 | -0.373 682 13 | -0.373 893 45 | -0.373 800 28 | -0.373 682 13 |
| 8.0 | 0.105 663 01 | 0.199 260 56 | -0.372 831 52 | -0.373 055 75 | -0.372 959 86 | -0.372 831 52 |

TABLE VI. Energy, geometry, dipole moment, and harmonic frequencies for H₂O calculated at M05/6-311++(2*d*,2*p*) with the unmodified and modified M05 XC functional (Ref. 5). Calculations done with Pople's 6-311++G(2*d*,2*p*) basis set (Ref. 9) and a (75,302) Euler/MacLaurin Lebedev grid (Refs. 11 and 12), unless stated otherwise.

| <i>a</i> (a.u.) | <i>E</i> (a.u.) | <i>r</i> (OH) (Å) | ∠(HOH) (deg) | μ (D) | ν ₁ (cm ⁻¹) | ν ₂ (cm ⁻¹) | ν ₃ (cm ⁻¹) |
|--------------------|--------------------|----------------------|-----------------|----------|---------------------------------------|---------------------------------------|---------------------------------------|
| 0 ^{a,b} | -76.422 552 1 | 0.9564 | 105.00 | 1.9619 | 1601.72 | 3898.04 | 4021.97 |
| 0 ^a | -76.422 535 5 | 0.9563 | 105.00 | 1.9616 | 1597.11 | 3895.14 | 4017.55 |
| 10 ⁻⁴ | -76.422 533 9 | 0.9563 | 105.00 | 1.9616 | 1597.12 | 3895.14 | 4017.55 |
| 10 ⁻³ | -76.422 526 2 | 0.9563 | 105.00 | 1.9617 | 1597.13 | 3895.14 | 4017.55 |
| 10 ⁻² | -76.422 769 2 | 0.9563 | 105.00 | 1.9621 | 1595.93 | 3895.01 | 4017.42 |
| 10 ⁻¹ | -76.426 702 5 | 0.9572 | 105.20 | 1.9535 | 1581.30 | 3879.53 | 4002.79 |
| 1 | -76.436 941 3 | 0.9567 | 105.33 | 1.9834 | 1572.70 | 3882.66 | 4006.39 |

^aUnmodified M05 functional.

^b(96,32,64) spherical grid (benchmark grid).

(75,302) and (99,590) grids, one finds convergence to spurious states for selected *R* values, which are remedied by the modification of the M05 functional. It should be noted that the convergence problems for the Na dimer follow a pattern: While in the region around the equilibrium, there are problems only for selected *R* values [*R*=6.6, 6.7 bohrs for (75,302) grid, *R*=6.4 bohrs for (99,590) grid], all calculations converge incorrectly or not at all for *R*>7.1 bohrs and the (75,302) grid and *R*>6.8 bohrs and the (99,590) grid. This behavior can be rationalized keeping in mind that the Na dimer is bound weakly and the highest occupied molecular orbital–lowest unoccupied molecular orbital energy difference is small and decreases rapidly with increasing *R*. Thus, for large *R*, the SCF procedure is sensitive to perturbations as, e.g., the spurious large contributions to the KS matrices discussed in this work. As an aside, we note that the total energies and equilibrium bond distance for Na₂ show a non-negligible variation with the grid size (see Table VI). This dependency reflects the insufficient resolution of commonly used production grids for meta-GGA calculations on weakly bound complexes.¹³

Similar problems were found in this work for K₂ and higher alkali dimers A₂, as well as their cations when described by pseudopotentials. One will come across the same problem for dynamical simulations of A_{*n*} clusters, despite the presence of occupied antibonding orbitals, due to the temporary formation of A₂ or A₃⁺ fragments. In the case of the all-electron investigation of the Li₂ dimer, SCF convergence problems do not occur since the core electrons generate a small but significant positive τ_σ value at the bond center, which prevents the KS matrix elements from becoming singular.

V. CONCLUSIONS

We have analyzed a convergence problem occurring for meta-GGA functionals such as VSXC,² TPSS,³ PKZB,⁴

M05,⁵ M05-2X,⁵ or M06-L.⁶ The problem was traced back to the way the self-interaction terms were eliminated in the equal-spin part of the correlation energy. We suggest a modified way for this elimination that avoids singularities in the KS matrix elements and resulting convergence problems, whereas leaving the XC energy values essentially unchanged. The modification suggested does not imply any substantial additional computational costs. In the case of the PKZB (Ref. 3) and TPSS (Ref. 4) functionals, an expression similar to *D*_σ is used for the self-interaction elimination, which has to be improved in the way described above.

ACKNOWLEDGMENTS

D.C. and D.I. thank the University of the Pacific for support.

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